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Relationship between the Schwinger and Kohn-type variational principles in scattering theory

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We establish the correct mathematical relationship between the Schwinger and Kohn variational principles for scattering theory and show that the Schwinger principle is one rank higher than the Kohn principle. If the same trial scattering wave function is used in these two principles, the Schwinger method should hence give superior results. Application of the Schwinger and Kohn variational principles to scattering by a simple model potential gives results which clearly illustrate this relationship.

I. INTRODUCTION

Kohn-type variational principles have been applied far more extensively to collision problems than the Schwinger variational principle. Historically, this has been due to the occurrence in the Schwinger variational principle of the term $\langle \Psi_{\mathbf{k}}^{(-)} | VG_0V | \Psi_{\mathbf{k}'}^{(+)} \rangle$ which has generally been regarded as difficult to evaluate in applications to realistic systems. This consideration seems to have outweighed some distinct advantages which the Schwinger variational principle is known to have.[1,2] Recent applications[3-5] have shown that the Schwinger variational principle is an effective approach to the electron-molecule collision problem. These applications to electron-molecule collisions and to a model two-channel problem[6] also demonstrated the very favorable convergence characteristics of the Schwinger method. For the model two-channel problem where a comparison with Kohn variational calculations was possible, our results revealed a superior convergence for the Schwinger method over the Kohn-type methods.[6] However, based on calculations for two model potentials, Thirumalai and Truhlar[7] and Callaway[8] recently concluded that the Kohn-type methods show much better convergence to accurate results than the Schwinger method. These results certainly suggest that it would be constructive to clarify the relationship between the Kohn and Schwinger variational methods and to interpret the results of these recent calculations[3,7,8] in the light of this relationship.

One of the objectives of this paper is to establish the explicit mathematical relationship between the Kohn and Schwinger variational principles since this relationship has not yet been well established. Kato[9] connected the Schwinger principle with the Rubinow method, which to our knowledge is the only direct relationship established between these two groups of variational principles. However, Kato[9] drew no conclusion concerning the relative convergence characteristics of these methods. Delves[10] commented briefly on the relationship between the Schwinger and Kohn methods, but we will show that the implied relationship between these two principles, which was assumed by Delves, is mathematically incorrect. In the next section we will derive a simple relationship between these two variational principles which shows that the Schwinger principle is one rank higher than the Kohn principle and, hence, with the same trial scattering wave functions will in general yield a superior result.

We will also present numerical results for scattering by the same model potential as that used in Ref. 7, but for which the same trial function is used in both the Schwinger and Kohn principles. These conclusions agree with the mathematical relationship which we will establish between these two methods. In the studies presented here the trial wave functions included long-range continuum functions since such functions are required in Kohn calculations. These continuum functions are not necessarily required in the Schwinger trial scattering function and, in fact, were not included in the model calculations of Refs. 7 and 8. Hence, their conclusion[7,8] that the Kohn method gives results superior to those of the Schwinger principle was based on model calculations in which different trial scattering wave functions were used in the different variational principles. An understanding of the role of continuum functions in trial scattering functions in the Schwinger method is necessary in the interpretation of these results. Calculations on a model potential will show that the range of the scattering potential determines the role of these continuum functions in Schwinger variational calculations.

II. RELATIONSHIP BETWEEN THE KOHN AND SCHWINGER VARIATIONAL PRINCIPLES

To our knowledge, an explicit quantitative relationship between the Kohn and Schwinger variational principles has not yet been established. To compare the convergence characteristics of these variational principles, we will first discuss some mathematical relationships between them.

The usual Kohn variational functional for the tangent of the phase shift λ,[11]

$$[\lambda]_K=\lambda+2\langle\Psi|\hat{H}|\Psi\rangle \tag{1}$$

can be written in the bilinear form[12]

$$\tfrac{1}{2}[\lambda]_K=\langle\tilde{C}|\hat{H}|\tilde{C}\rangle-\langle\tilde{C}|V|S\rangle -\langle S|V|\tilde{C}\rangle-\langle S|V|S\rangle\,, \tag{2}$$

where $\hat{H}=E-H$, S is the regular solution of the unperturbed Hamiltonian $H_0=H-V$, and Ψ is the trial wave function which can be written as

$$\Psi=\tilde{C}+S\,, \tag{3}$$

with

$$\tilde{C}=\lambda C+\sum_i a_i\eta_i\,. \tag{4}$$

In Eq. (4) for s-wave scattering

$$C\sim\begin{cases}k^{-1/2}\cos(kr) & \text{as } r\to\infty\\ 0 & \text{as } r\to 0\,,\end{cases} \tag{5}$$

and η_i is a discrete basis function. One can generalize the functional in Eq. (2) and write

$$I(\phi,\psi)=\langle\phi|\hat{H}|\psi\rangle-\langle\phi|V|S\rangle -\langle S|V|\psi\rangle-\langle S|V|S\rangle\,. \tag{6}$$

A systematic way to select the trial wave functions ϕ and ψ is as follows. The exact function $\tilde{C}$ of Eq. (4) satisfies a Lippmann-Schwinger equation of the form[12]

$$\tilde{C}=G_0VS+G_0V\tilde{C}\,. \tag{7}$$

This integral equation can be solved by the iterative procedure[1,4,13]

$$\tilde{C}_{n+1}=G_0VS+G_0V\tilde{C}_n\,. \tag{8}$$

We select $\tilde{C}_1$ to be given by the expansion in Eq. (4) and insert this function into the variational functional of Eq. (6). Then we have

$$[\lambda]_K=2I(\tilde{C}_1,\tilde{C}_1)\,. \tag{9}$$

Therefore the functional $2I(\tilde{C}_1,\tilde{C}_1)$ is just the tangent of the phase shift as given by the Kohn variational principle. Next, we consider the higher-rank variational functional $I(\tilde{C}_1,\tilde{C}_2)$. Some simple manipulation shows that

$$I(\tilde{C}_1,\tilde{C}_2)=\langle\Psi_1|(V-VG_0V)|\Psi_1\rangle -\langle\Psi_1|V|S\rangle-\langle S|V|\Psi_1\rangle\,, \tag{10}$$

where $\Psi_1=S+\tilde{C}_1$. The right-hand side of Eq. (10) is just the bilinear form of the Schwinger variational functional. Therefore we have

$$[\lambda]_S=2I(\tilde{C}_1,\tilde{C}_2)\,. \tag{11}$$

If the trial function $\tilde{C}_1$ is good enough so that the iterative procedure converges montonically, a higher-rank functional $I(\tilde{C}_m,\tilde{C}_n)$ should give a more accurate result than any lower-rank functional. Since the functionals $I(\tilde{C}_1,\tilde{C}_2)$ and $I(\tilde{C}_1,\tilde{C}_1)$ correspond to the Schwinger and Kohn variational principles, respectively, this shows that for a given trial function, the Schwinger variational principle yields a more accurate result than does the Kohn principle. Explicitly one can examine the second-order terms arising in the functional $I(\phi,\psi)$ when ϕ and ψ are varied about their exact values and show that these terms are smaller for the Schwinger functional than for the Kohn functional.

Some years ago Delves[10] stated without any proof that the output from the Schwinger principle $[\lambda]_S$ with the trial function $\Psi^{(1)}$ is identical with the output from the Kohn principle $[\lambda]_K$ with the trial function $\Psi^{(2)}$, where

$$\Psi^{(2)}=S+G_0V\Psi^{(1)}\,. \tag{12}$$

Although the realization of the relationship Eq. (12) is important, the statement itself is not correct. The output from the Kohn principle with $\Psi^{(2)}$ corresponds to the functional $I(\tilde{C}_2,\tilde{C}_2)$ and not $I(\tilde{C}_1,\tilde{C}_2)$ in our proof. In fact, $I(\tilde{C}_2,\tilde{C}_2)$ is equivalent to a higher-order functional

$$F_0=\frac{|\Psi|VG_0V|S\rangle\langle S|VG_0V|\Psi\rangle}{\langle\Psi|VG_0V-VG_0VG_0V|\Psi\rangle} \tag{13}$$

which we have discussed previously and has also been stated by Newton.[14] Finally, we note that some of the functionals $I(\tilde{C}_m,\tilde{C}_n)$ for $m,n\geq 2$ correspond to different steps in the iterative Schwinger method.[4]

These arguments rigorously establish the mathematical relationship between the Kohn and Schwinger variational principles. Some additional insight into the relative convergence characteristics of these two methods can be obtained by looking at the approximations implied in the solution of the Lippmann-Schwinger equation for the K matrix in these two methods. Although some of these relationships are well known, a brief discussion of them here is very relevant. The Schwinger variational expression for the tangent of the phase shift is equivalent to the exact solution of the Lippmann-Schwinger equation for the

K operator[15]

$$K = V + VG_0K \,, \tag{14}$$

with V replaced by the finite-rank approximation

$$V^S = \sum_{i,j} V|\chi_i\rangle(v^{-1})_{ij}\langle\chi_j|V \,, \tag{15}$$

where $v_{ij} = \langle\chi_i|V|\chi_j\rangle$ and χ_i is a basis function. It is well known that the separable form of the potential in Eq. (13) is exact within the space spanned by the functions $\{\chi_i\}$, i.e.,

$$V^S|\chi_i\rangle = V|\chi_i\rangle \,. \tag{16}$$

On the other hand, the Kohn variational expression for the tangent of the phase shift is equivalent to solving a variant of the Lippmann-Schwinger equation[12]

$$f = VG_0V + VG_0f \,, \tag{17}$$

with

$$f = K - V \,, \tag{18}$$

using the finite-rank Green's function

$$G_0^S = \sum_{ij} |\chi_i\rangle(B^{-1})_{ij}\langle\chi_j| \,, \tag{19}$$

where

$$B_{ij} = \langle\chi_i|G_0^{-1}|\chi_j\rangle = \langle\chi_i|(E - H_0)|\chi_j\rangle \,. \tag{20}$$

This finite-rank Green's function does not satisfy the relationship which V^S satisfies in Eq. (16), i.e.,

$$G_0^S|\chi_i\rangle \neq G_0|\chi_i\rangle \,. \tag{21}$$

Finite-rank approximations to operators which obey the relationship given in Eq. (16) are generally expected to be better approximations to the operator than those finite-rank approximations which do not have this property. Further, we note that this approximation to the Green's function in the Kohn principle is the origin of its spurious singularities.[16] These observations again suggest that the Schwinger variational principle should have better convergence characteristics than the Kohn principle.

III. DIRECT COMPARISON OF THE KOHN AND SCHWINGER VARIATIONAL PRINCIPLES

To give a numerical comparison of the convergence of the Kohn and Schwinger variational principles we have carried out calculations on the same model system as that used by Thirumalai and Truhlar.[7] However, in contrast to their studies,[7] we have used the same trial scattering wave function in the two variational principles.

The scattering potential is the attractive exponential potential

$$V(r) = -e^{-r} \tag{22}$$

and we consider only s-wave scattering. All comparisons are made in terms of the K matrix element, i.e., $\tan\delta_0$. The trial scattering function used in both the Schwinger and Kohn variational principles in these studies is

$$\Psi(t) = X^n(r)/r \,, \tag{23}$$

with the function $X(r)$ of the form

$$X^n(r) = \alpha_0 \sin kr + \alpha_1(1 - e^{-\beta r})\cos kr + \sum_{a=1}^{n} C_a r^a \exp(-\alpha r) \,, \tag{24}$$

where if $n = 0$, no discrete basis functions are included in the trial function. In all results presented here we also choose $\alpha = 2.5$ and $\beta = 1.0$.[7]

In Tables I–III we compare the results obtained with the trial function of Eq. (24) in the Schwinger variational principle with the results of several other variational methods considered by Thirumalai and Truhlar.[7] These include the anomaly-free (AF)[17] and optimized anomaly-free (OAF) adaptations of the Kohn methods[18] and the minimum-norm-Kohn (MNK),[19] minimum-norm-inverse-Kohn (MNR),[11(a)] and optimized-minimum-norm (OMN)[18] versions of the Harris-Michels-type methods. From the results at these three ener-

TABLE I. Ratio of variational K matrix elements to the accurate value for $k = 0.55$ a.u.[a]

n[b]	AF[c]	OAF	MNK	MNR	OMN	Schwinger[d]
0	0.9735	0.9733	0.9733	0.9735	0.9733	0.9972
2	0.9968	0.9940	0.9902	0.9969	0.9941	0.9999
4	0.9999	0.9970	0.9910	0.9999	0.9970	1.0000

[a] Accurate value is $K_0 = 2.200\,382\,7$.

[b] The number of discrete basis functions in the trial function [see Eq. (24)]. For $n = 0$ no discrete basis functions are included in the trial function.

[c] The results in the AF, OAF, MNK, MNR, and OMN columns are from Ref. 7 except those for $n = 0$ which are from Ref. 11(a).

[d] Results from the Schwinger variational principle.

TABLE II. Ratio of variational K matrix elements to the accurate value for $k=0.35$ a.u.[a]

n	AF	OAF	MNK	MNR	OMN	Schwinger
0						0.9765
2	0.9879	0.9858	0.9622	0.9902	0.9861	0.9999
4	0.9980	0.9978	0.9878	0.9980	0.9978	1.0000

[a] Accurate value is $K_0=9.091\,809\,5$. See also footnotes in Table I.

gies the Schwinger variational principle clearly yields superior results to those of the Kohn and Harris-Michels methods. These results are not unexpected and are consistent with the mathematical relationship between these variational principles which we established in the previous section of this paper.

A comparison of the results of Ref. 7 in which only discrete basis functions were used in the Schwinger calculations and the present results shows that the inclusion of continuum functions in the Schwinger trial function can be very effective. For example, with a trial function containing only two discrete basis functions in the Schwinger principle at $k=0.55$ a.u., Thirumalai and Truhlar[7] obtained a ratio of the tangent of the phase shift to the accurate value of 0.6063. If the continuum functions $\sin kr$ and $\cos kr$ are added to this two term basis, the Schwinger variational principle yields a value of 0.9999 for this same ratio. From Table 3 of Ref. 7, about 12 to 14 discrete functions are required to obtain such an accurate value if the continuum functions are not included in the trial function. In our previous studies of the scattering of electrons by molecules with long-range potentials we also find that the inclusion of continuum functions in the trial function can be very effective.[4,5] We have developed the iterative Schwinger variational method[4] as one way to systematically include continuum trial functions in the Schwinger variational principle when necessary.

We believe that such continuum functions play their most important role in the region intermediate between the short-range region, where discrete basis functions are very effective, and in the asymptotic region. This would suggest that the need to include continuum functions in the Schwinger method is affected by the relationship between the range of the potential and the effective range of the L^2 functions included in the trial scattering function.

To obtain some insight into these relationships we look at s-wave scattering in the following cutoff potential:

$$V_R(r)=\begin{cases}-\exp(-r)\,, & r\leq R\\ 0\,, & r>R\,.\end{cases} \tag{25}$$

In Table IV we present the results of calculations for this potential in which the cutoff distance R is systematically increased. The K matrix elements in this table are obtained with a trial function containing only four discrete basis functions. These results show that, for $R<4$ a.u., this purely L^2 basis set gives results within 1% of the accurate values which were obtained by direct numerical integration. For values of R greater than $R=4$ a.u., which we loosely define as the beginning of the intermediate region for this basis set, the results show that this same basis can no longer provide an adequate representation of the scattering function. For all the cutoff potentials shown in Table IV, a trial function containing the continuum functions in addition to these four L^2 functions, i.e., $X^4(r)$ of Eq. (24) gives the accurate values. These results show that the regular and regularized irregular continuum functions together can provide an accurate representation of the wave function in the intermediate region.

IV. CONCLUDING REMARKS

Our main purpose has been to clarify the relationships between the Kohn and Schwinger varia-

TABLE III. Ratio of variational K matrix elements to the accurate value for $k=0.15$ a.u.[a]

n	AF	OAF	MNK	MNR	OMN	Schwinger
0						1.0124
2	1.0005	1.0009	1.0004	1.0010	1.0009	1.0000
4	1.0006	1.0004	1.0002	1.0005	1.0004	1.0000

[a] Accurate value is $K_0=-1.744\,939\,3$. See also footnotes in Table I.

TABLE IV. s-wave Schwinger K matrix elements for the potential of Eq. (25) at $k=0.55$ a.u.

R(a.u.)[a]	$\tilde{K}_0$[b]	$\tilde{K}_0/K_0$[c]
1.0	0.262 65	1.0000
2.0	1.449 33	0.9991
3.0	2.028 61	0.9968
4.0	2.047 80	0.9935
5.0	2.039 75	0.9711
6.0	2.038 53	0.9447
20.0	2.038 43	0.9264

[a] Value of the cutoff radius in the potential of Eq. (25).
[b] Schwinger variational result of four discrete basis functions with $\alpha=2.5$.
[c] Ratio of the K matrices in the preceding column with accurate values.

tional principles. We have obtained the explicit mathematical relationship between these two stationary principles which shows that the Schwinger variational principle is one rank higher than the Kohn principle and hence, if the same trial scattering wave function is used in these two principles, the Schwinger principle should lead to a superior result. We have also shown that the relationship between these principles stated earlier by Delves[10] is incorrect. We have carried out calculations on the same model potential as Thirumalai and Truhlar[7] and have shown that these results confirm the relationship that the Schwinger principle is of a higher rank. We have also shown that the accuracy of a Schwinger calculation with a basis containing only discrete functions is strongly affected by the range of the potential. Thus a comparison of the Kohn and Schwinger principles with different trial functions will also depend on the range of the potential.

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